

FEDERAL REPUBLIC
OF GERMANY

(12) Offenlegungsschrift

(51) Int.Cl.³:
C 08 F 14/06

(11) DE 30 11 645 A-1

(21) Application no.: P 30 11 645.1
(22) Application date: 3/26/80
(43) Date of opening for
public inspection: 10/1/81

GERMAN PATENT
OFFICE

(71) Applicant:

Henkel KGaA, 4000 Düsseldorf,
DE

(72) Inventor(s):

Höfer, Rainer, Dipl.-Chem.,
Dr., 4000 Düsseldorf, DE;
Erwied, Werner, Dipl.-Chem.,
Dr., 4018 Langenfeld, DE;
Wegemund, Bernd, Dipl.-Chem.,
Dr., 5657 Haan, DE;
Eckelt, Michael, 4000
Düsseldorf, DE

"mixed esters" used as dispersion aids

(54) Dispersion aid for the polymerization of vinyl chloride and
its use

Claims



1. Use of mixed esters of a hydroxycarboxylic acid with up to 6 C atoms and

- a) partial esters of saturated or olefinically unsaturated monocarboxylic acids with 10 to 24 C atoms, which may also be substituted with a hydroxyl group and polyols with 3 to 6 C atoms and at least 3 OH groups or
 - b) esters of the monocarboxylic acids according to a) with hydroxycarboxylic acids with up to 6 C atoms
- as dispersion aids for the polymerization of vinyl chloride.

2. Embodiment in accordance with Claim 1, characterized in that mixed esters of hydroxycarboxylic acid with 3 to 6 C atoms are used, which preferably contain 1 to 3 carboxyl groups and 1 or more hydroxyl groups.

3. Embodiment in accordance with Claims 1 and 2, characterized in that mixed esters are used which contain residues of straight chain or branched monocarboxylic acids with preferably 12 to 18 C atoms.

4. Embodiment in accordance with Claims 1 to 3, characterized in that mixed esters are used which for each mol-part of hydroxycarboxylic acid preferably contain 0.5 to 1 mol-part, preferably about 1 mol-part, of the partial ester in accordance with Claim 1a) or the ester in accordance with Claim 1b).

5. Exemplified embodiment in accordance with Claims 1 to 4, characterized in that mixed esters in accordance with Claim 1b) are used, which in the molecule have the same or different residues of hydroxycarboxylic acids with up to 6 C atoms.

6. Exemplified embodiment in accordance with Claims 1 to 5, characterized in that the mixed esters are used at pH values of 4 to 10, especially 6 to 8, possibly in the form of their water-soluble salts.

7. Embodiment in accordance with Claims 1 to 6, characterized in that the mixed esters are used together with the usual protective colloids for the suspension polymerization of vinyl chloride, especially together with polyvinyl alcohols or cellulose ethers.

VON KREISLER SCHÖNWALD EISHOLD FUES
VON KREISLER KELLER SELTING WERNER

PATENT ATTORNEYS

Dr.-Eng. von Kreisler- 1973
Dr.-Eng. K. Schönwald, Cologne
Dr.-Eng. K.W. Eishold, Bad Soden
Dr. J. F. Fues, Cologne
Certif. Chemist Alek von Kreisler, Cologne
Certif. Chemist Carola Keller, Cologne
Certif. Eng. G. Selting, Cologne
Dr. H.-K. Werner, Cologne

Deichmannhaus am Hauptbahnhof
D-5000 Cologne 1

March 25, 1980
Fu/Pf/Bf

Henkel KGaA, Henkelstrasse 67, 4000 Düsseldorf 1.

**Dispersion aid for the polymerization of vinyl chloride
and its use**

D 6015

Vinyl chloride can be prepared industrially according to the known methods of bulk, solution, emulsion, and suspension polymerization. Among these methods, polymerization in suspension is characterized by various advantages: low processing costs, good process control, and good optical properties, high chemical resistance and low foreign matter content of the polymer. The easy-to-perform isolation by filtration or centrifugation gives a free-flowing powder.

Regarding the relevant literature see, for example, *Encyclopedia of PVC*, Vol. 1, pages 76-85, edited by L.I. Nass, Marcel Dekker, New York, Basel (1976) or *Developments in PVC Production and Processing -1*, pages 13-42, edited by A. Whelan and J.L. Craft, Applied Science Publishers Ltd., London (1977).

For suspension polymerization, the water-insoluble monomeric vinyl chloride, liquid under pressure at room temperature, is dispersed in one to four times its volume of purified water by intensified agitation into small drops, and polymerized to completion in this form, yielding small polymer beads. Indispensable for the formation of stable suspensions is the addition of a suspension agent, a protective colloid, or another surface-active agent to the water/monomer mixture. Originally for stabilization of the monomer droplets, inorganic solids were used (talcum, hydrargillite, magnesium hydroxide, calcium phosphate), which collect at the monomer/water interface and thus prevent caking together of the vinyl chloride beads. Today for this purpose hydrophilic macromolecules are generally used, e.g., polyvinyl alcohols, cellulose derivatives, copolymers of maleic acid or its anhydride or imide with styrene, vinyl acetate, vinyl ethers or ethylene, hydrolyzed vinyl acetate-styrene copolymers, polyvinylpyrrolidone and copolymers, gelatins, starches, alginates, polymeric phosphates, and combinations of these substance groups.

The selection and composition of the suspension system has a decisive influence on the quality of the crude PVC product. In particular, the following parameters of importance for application are determined in advance during polymerization: bulk density, particle size, particle size distribution, plasticizer uptake, plasticizer uptake rate, optical properties, electrical properties, heat resistance. At the same time, insofar as possible, already through the selection of the suspension agent system, inhomogeneities in the particles (which can be noticed as stipples or fish-eyes after plasticization) and wall deposits in the polymerization reactor can be ruled out.

The addition of emulsifiers during suspension polymerization serves to influence the morphology of the PVC grain, which is ultimately of determining significance for the bulk density and the plasticizer uptake capacity. Both parameters, although antagonistic, should be as high as possible, the bulk density for economic reasons and the plasticizer uptake for processing technology reasons. Optimal properties can only be expected when a defined, narrow particle size distribution is achieved in the polymerization process, a fact to which the emulsifier is also supposed to contribute.

As auxiliary dispersants in this sense, to improve individual effects, a number of surface-active compounds have already been investigated. For example, US Patent 2,528,469 describes the addition of dioctyl sulfosuccinate, while British Patent 755,796 recommends among other things the use of fatty acid monoglyceride-ethylene oxide condensation products, DE-AS 1,076,374 the use of esters of an aliphatic polyhydric alcohol and an unsaturated polyhydroxy fatty acid, and DE-AS 1,105,616 the use of triglycerol monostearate.

The present invention has taken on the task of using a group of emulsifiers for the suspension polymerization of vinyl chloride which act in combination with a conventional protective colloid as a dispersion aid and which give the PVC in particular a narrow particle size distribution, a high porosity, and along

with this a high plasticizer uptake with simultaneously a high bulk density. It was found that certain mixed esters defined in the following are suitable for carrying out the process in accordance with the invention.

Correspondingly the subject of the invention is the use of mixed esters of hydroxycarboxylic acids with up to 6 C atoms and (a) partial esters of monocarboxylic acids with at least 10 C atoms and polyols with 3 to 6 C atoms and at least 3 OH groups or b) esters of the monocarboxylic acids according to a) with hydroxycarboxylic acids with up to 6 C atoms as dispersion aids for the polymerization of vinyl chloride.

The mixed esters used in accordance with the invention can be employed as anionic or nonionic complex esters, wherein the anionic form as a rule is characterized by the presence of non-esterified carboxyl groups.

Therefore in accordance with the invention two classes of mixed complex esters are suggested which if desired may also be used in combination with one another or in combination with other dispersion aids. It is simultaneously true for these two classes that as a rule they are made up of three basic components. In both cases as the first basic component of the mixed ester, hydroxycarboxylic acids with up to 6 carbon atoms are present. These hydroxycarboxylic acids can have one or more carboxyl groups, wherein preferably 1 to 3 carboxyl groups are present. It is correspondingly true for the hydroxyl groups that here also one or more hydroxyl groups may be present, wherein here likewise 1 to 3 hydroxyl groups, especially 1 or 2 hydroxy groups, may be particularly preferred. Particularly suitable hydroxycarboxylic acids contain 3 to 6 C atoms. Within the framework of the invention the following hydroxycarboxylic acids have particular significance:



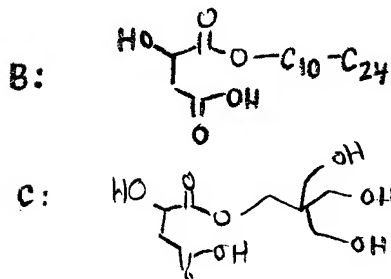
lactic acid, tartronic acid (hydroxymalonic acid), glycerol carboxylic acid, tartaric acid, malic acid and especially citric acid.

In the following, for simplicity's sake these hydroxycarboxylic acid components will be designated as A. Depending on the specific structure of the complex or mixed ester, they are bound into the mixed ester over a carboxylic acid group or over a hydroxyl group.

In the previously described embodiment according to (a), the hydroxycarboxylic acid (A) is bound over its carboxyl group or one of its carboxyl groups in ester form with a partial ester of monocarboxylic acids with at least 10 C atoms - designated by B ^{C₁₀⁺ esters} in the following - and polyols with 3 to 6 C atoms and at least 3 OH groups - designated in the following as C. In the first class of dispersion aids used in accordance with the invention described here, therefore the mixed ester is made up overall of the hydroxycarboxylic acid A, the monocarboxylic acid B, and the polyol C. Specifically the following information is applicable to the components B and C that form the partial ester:

The monocarboxylic acid (B) generally have 10 to 24 C atoms, while the particularly preferred range is 12 to 18 C atoms. The acids are preferably straight-chain or branched and can be saturated or olefinically unsaturated. If unsaturated acids are present, singly unsaturated acids are preferred, but multiply unsaturated acids - for example, those with 2 or 3 olefinic double bonds - are not ruled out. Typical representatives for acids of the type involved here come from the class of fatty acids. It is also possible that these monocarboxylic acids in accordance with B be hydroxylated, preferably singly.

In the first class of dispersion auxiliaries described here, these monocarboxylic acids form partial esters with polyols with 3 to 6 C atoms and at least 3 OH groups - component C. These polyols in turn may be straight-chain or branched. Examples of straight-chain polyols are glycerol, pentoses or hexoses, for example sorbitol or mannitol, although glycerol has particular significance here. Example of branched polyols of this type are pentaerythritol or trimethylol propane. Particular significance



is attached to pentaerythritol within the framework of the teaching of the invention.

In the partial esters B + C the mixing ratio of B to C is usually in the range of 1 to 3:1 to 1:1. The range of 1 to 2:1 is preferred, and especially the equimolar mixing ratio of 1:1.

The molar ratio of the hydroxycarboxylic acids (A) to the partial esters (B + C) preferably falls in the range of 2:1 to 1:1, wherein here also molar ratios in the range of about 1:1 are particularly preferred. In the particularly preferred embodiment of the invention therefore the components A : B : C fall in the range of about 1:1 to 2:1.

Free hydroxy groups, for example those from component A, can be esterified with short-chain carboxylic acids, for example those with 1 to 3 C atoms. Free carboxyl groups can be present as such, but they can also be provided in the form of their water-soluble salts, especially corresponding alkali or alkaline earth salts.

In the second embodiment of the invention, mixed or complex esters according to (b) consisting of the previously mentioned hydroxycarboxylic acid esters A and esters formed by reaction of monocarboxylic acids according to B with hydroxycarboxylic acids with up to 6 C atoms are used. For these hydroxycarboxylic acid constituents of the mixed ester as well, the general and specific statements previously made regarding A are applicable. In this second embodiment of the invention therefore, in the general case, together with one part of the monocarboxylic acid B, two parts of hydroxycarboxylic acids according to A are present. These hydroxycarboxylic acid constituents can be derived from the same or different hydroxycarboxylic acids, but the statements regarding A apply for both constituents. It is also true here that free hydroxyl groups may be esterified with lower carboxylic acids with 1 to 3 C atoms and that any free carboxyl groups present can also be converted to water-soluble salts. Here and in the case of the mixed esters of the first class, the use of

these dispersion aids at pH values of 4 to 10, especially 6 to 8, is preferred.

Emulsifiers of the type described here are at least partially known; they are used among other things as baking aids. Their preparation has been described, for example, for complex esters of fatty acids, glycerol, and fruit acids, for example in German Patent 1,278,423 and German OS 2,732,210 and 2,734,059. The fact that their use in the area of polymerization of vinyl chloride especially by the suspension method leads to particularly advantageous process products, however, could not be predicted.

The anionic and nonionic complex esters used in accordance with the invention are usually used in quantities of 0.005 to 0.5 wt%, especially of 0.01 to 0.3 wt%, based on the monomer to be polymerized. In this process the mixed and complex esters described here are usually used in combination with conventional protective colloids. Protective colloids in the sense of the invention are especially polyvinyl alcohols, which from the time of their manufacturing still may contain variable amounts of acetyl groups. However, improvements in the process product are also observed when cellulose derivatives are used as the protective colloid.

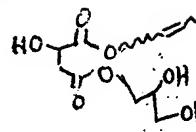
As monomer-soluble catalysts in the process falling within the framework of the invention for polymerization of vinyl chloride, the following can be used: Peroxides, such as benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, lauroyl peroxide, azo compounds such as azoisobutyrodinitrile, azo-bis-dimethylvalerodinitrile, or peresters such as tert-butylperpivalate, specifically in quantities of 0.01 to 0.3 parts based on 100 parts of the monomer. The previously mentioned conventional protective colloids can be used in quantities of 0.01 to 0.5 wt%, based on the monomer to be polymerized. Additional possible additives that may be recommended during the performance of polymerization are buffer substances, e.g., phosphates, the quantity of which

should be selected such that the pH of the aqueous phase is between 4 and 10, preferably between 6 and 8.

Advantageously the complex esters and possibly the buffer substances are added before the beginning of polymerization. However, the procedure followed may also be such that the polymerization is initiated normally and the dispersion aid is introduced all at once after a certain reaction time or gradually into the reaction vessel. The polymerization can be performed at conventional temperatures between 30 and 75°C, preferably between 40 and 70°C.

The use of up to 20 wt% comonomers for producing copolymers is possible. As comonomers for producing copolymers, ethylene, propylene, vinyl acetate, vinylidene chloride, vinyl ether, acrylonitrile, or acryl esters come under consideration.

Complex and mixed esters of the previously described first group that are suitable in accordance with the invention are for example the following compounds: mono-^{C₁₈ (unsat)}oleyl-glyceride-lactate, mono-^{C₁₆}ricinoleoyl-glyceride-lactate, mono-^{C₁₈}palmitoyl-glyceride-lactate, mono-isopalmitoyl-glyceride-lactate, mono-stearoyl-glyceride-lactate, mono-isostearoyl-glyceride-lactate, mono-hydroxy-stearoyl-glyceride-lactate, the mixed esters analogous to the previously mentioned compounds in which the glycerol has been replaced by pentaerythritol or sorbitol, the compounds homologous to the above-mentioned compounds in which the lactate radical is replaced by the citrate radical, the malate radical, or the tartrate or diacetyltartrate radical. In the case of the glycerol-containing and also pentaerythritol-containing partial esters, dipartial esters may also be present in addition to or in place of the monopartial ester.



Examples of dispersion auxiliaries of the above-described second class are as follows: oleoyl-lactoyl-lactate, ricinoleoyl-lactoyl-lactate, palmitoyl-lactoyl-lactate, isopalmitoyl-lactoyl-lactate, stearoyl-lactoyl-lactate, hydroxystearoyl-lactoyl-lactate, isostearoyl-lactoyl-lactate, the mixed esters corresponding to the above-mentioned compounds in which the

monocarboxylic acid according to B is esterified with citric acid, malic acid, or tartaric acid, and the compounds homologous to the above-mentioned compounds in which the lactate radical is replaced by the citrate radical, malate radical, or the tartrate radical.

Example

800 g deionized water, 500 g vinyl chloride, 0.125 g sodium hydrogen carbonate, 2.5 g lauroyl peroxide, and a mixture, presented in greater detail in the following table, of protective colloid and dispersion aid, were heated in a V2A agitator autoclave under vigorous agitation to 55°C. After 7 to 8 hr the pressure in the autoclave dropped to about 4.6 bar. The polymerization was then ended and polyvinyl chloride filtered from the suspension by suction, washed with water and methanol, and dried under vacuum at 50°C.

In the Tables that follow the properties of the polymers obtained are listed. The properties are compared with the properties of a PVC that was produced without addition of auxiliary dispersant and with a PVC that contained as the dispersion sorbitan monooleate as the relative state of the art.

TABLE I

Example	Protective colloid	Concentration (%) based on the monomer	Dispersion aid	Concentration (%) based on the monomer
1	PVAL ¹	0.3	--	--
2	PVAL	0.3	Sorbitan monooleate	0.1
3	PVAL	0.3	Monostearoyl glyceride-citrate	0.1
4	PVAL	0.3	Na-stearoyl-lactoyl-lactate	0.01
5	PVAL	0.1	--	--
6	PVAL	0.1	Sorbitan monooleate	0.01
7	PVAL	0.1	Na-stearoyl-lactoyl-lactate	0.01
8	PVAL	0.1	Ca-stearoyl-lactoyl-lactate	0.01

¹A commercial partially saponified polyvinyl alcohol with a viscosity (4% aqueous solution at 20°C) between 30 and 60 mPa·sec.

TABLE II

Example	Plasticizer uptake acc. to DIN 53417, part 1, in g DOP/100 g PVC	Bulk density acc. to DIN 53468	Coating (%)	Heat stability acc. to DIN 53418 (180°C), in min*
1	19.3	550	< 3	60
2	20.6	529	< 3	80
3	23.1	527	< 3	100
4	23	526	< 3	80
5	16.2	556	low	60
6	16.4	586	0	80
7	18	524	0	80
8	21.3	515	0	80

*Formulation: 100 parts by weight PVC
1.5 parts by weight organotin stabilizer (Irgastab 17 MOK,
Ciba Geigy Co.)

TABLE III

Examp le	Screen analysis (%)					Particle size distribution (%)*
	0.8 mm	0.4 mm	0.2 mm	0.1 mm	0.5 mm	
1	0.4	59.6	24.6	9.9	5.3	34.5
2	0	4.4	60.4	22.5	12.8	82.9
3	0.5	2.7	85.8	9.7	0.4	95.5
4	0.4	3.9	51.9	40.0	4.4	91.9
5	0	1.8	38.7	49.9	9.0	88.6
6	0	3.0	49.7	41.0	6.2	90.7
7	0.3	1.2	69.0	28.5	1.0	97.5
8	0.3	0.9	66.2	32.1	0.5	98.3

*Fraction of PVC grains of $0.4 < d \leq 0.1 \text{ mm}$

